

**JAPANESE**

[JP,11-268187,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD  
PRIOR ART EFFECT OF THE INVENTION TECHNICAL  
PROBLEM MEANS EXAMPLE

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the fluororesin sheet which has an adhesive property on the glass for obtaining the layered product of glass and a fluororesin sheet, and its layered product.

[0002]

[Description of the Prior Art]Although a glass plate is a material which has transparency and intensity, its shock resistance is weak, and generally the safety glass pasted together to the plastic sheet is used as the method of compensating it. However, although scattering of a fragment when glass breaks can be prevented, since a plastic sheet burns in case of a fire, fire retardancy cannot be satisfied to a common plastic sheet. Then, even if it has fire prevention and flame-resistance and is usually sometimes divided, the fire prevention safety glass which pasted up the fluororesin sheet on the glass plate is proposed as glass which has fragment preventing scattering.

[0003]However, since the fluororesin sheet was lacking in other

materials, such as glass, and an adhesive property, when it was going to attain firm adhesion, it was necessary but to use adhesives, and it was difficult to attain firm adhesion anyway.

[0004]Although a polyvinyl butyral, an ethylene-vinylacetate copolymer, etc. are used as an interlayer for manufacturing a glass laminate conventionally, firm adhesion cannot be attained even if it applies such materials to adhesion with a fluororesin sheet and glass.

[0005]

[Problem(s) to be Solved by the Invention]This invention carries out the purpose of providing the new fluororesin sheet for lamination for obtaining the glass which solved the aforementioned problem, the new layered product which the fluororesin sheet pasted up firmly, and such a layered product.

[0006]

[Means for Solving the Problem]The aforementioned purpose is attained by the following means. Namely, this invention is what proposes a glass layered product pasting up glass and a fluororesin sheet via an acrylic ester copolymer which replaced a part of polymethylmethacrylate by amino alkyl (meta) acrylate at least, A fluororesin sheet for glass lamination providing an acrylic ester copolymer tunic which replaced a part of polymethylmethacrylate at least by one side of a fluororesin sheet by amino alkyl (meta) acrylate at least is proposed.

[0007]

[Embodiment of the Invention]Hereafter, this invention is explained in more detail.

[0008]A monomer component the fluororesin sheet in this invention Vinyl fluoridation. Vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, The homopolymer or copolymers of a fluorine-containing monomer, such as pentafluoropropylene and hexafluoropropylene, Or it becomes said fluorine-containing monomer from the copolymers in which vinyl monomers, such as ethylene and alkyl vinyl ether, etc. were used together, or these mixtures.

[0009]And what can be fabricated to a sheet shaped, i.e., thermofusion shaping, should be just possible, and fluoro-resins other than the homopolymer (PTFE) of tetrafluoroethylene can be especially used without restriction.

[0010]Specifically A tetrafluoroethylene perphloro alkyl vinyl ether copolymer, A tetrafluoroethylene ethylenic copolymer, a tetrafluoroethylene hexafluoropropylene copolymer, A tetrafluoroethylene vinylidene fluoride hexafluoropropylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, etc. are mentioned. And when making fireproof glass profitably like, in order to secure fire retardancy, it is preferred that the content of

fluoride chooses 60% of the weight or more of a thing preferably 55% of the weight or more.

[0011]As this fluororesin sheet, what contains vinylidene fluoride as an ingredient for the below-mentioned reason is preferred. As a desirable fluororesin sheet, vinylidene fluoride, tetrafluoroethylene, and the 3 yuan copolymer of hexafluoropropylene are mentioned especially. The desirable copolymerization ratios of this 3 yuan copolymer are 20 to 40 % of the weight of vinylidene fluorides, 20 to 60 % of the weight of tetrafluoroethylenes, and 5 to 20 % of the weight of hexafluoropropylene.

[0012]Crystallinity is low, the sheet of this copolymer has good transparency, it is flexible, and it is excellent in shock resistance, and since the melting point is comparatively low, it fits thermal melting arrival with glass.

[0013]Although the thickness in particular of a fluororesin sheet is not restricted, when the influence etc. which it has on shock resistance when it laminates with glass are taken into consideration, the range of 50-2000 micrometers is preferred.

[0014]Shaping of a fluororesin sheet should just be based on the method generally known, for example, a fluoro-resin is dissolved in an organic solvent, How to carry out dry removal of the organic solvent, remove from a substrate, and sheet-ize after applying uniformly on a detachability substrate, After applying the drainage system dispersion of a fluoro-resin uniformly on the substrate of detachability, the method of sheet-izing with thermoplastic shaping of the method of drying water or an extrusion method, the calendar method, etc., etc. are possible.

[0015]In this fluororesin sheet, various additive agents can be added within limits which do not spoil the characteristic of a fluororesin sheet, especially transparency.

[0016]the adhesive film for pasting up this fluororesin sheet with glass -- at least one side of a fluororesin sheet -- it is suitably provided in both sides. It may form in a glass surface.

[0017]The adhesives which form an adhesive film are the acrylic ester copolymers which replaced a part of polymethylmethacrylate by amino alkyl (meta) acrylate at least. As amino alkyl (meta) acrylate, (Meta) Acrylic acid aminomethyl, acrylic acid (meta) beta-aminoethyl, (Meta) Acrylic acid gamma-aminopropyl, acrylic acid (meta) N-(beta-aminoethyl)-gamma-aminopropyl, (Meta) Acrylic acid N,N-dimethylaminoethyl, an acrylic acid (meta) N,N-diethylaminoethyl, acrylic acid (meta) t-butylamino ethyl, acryloyloxyethyl (meta) isocyanurate, (Meta) Acryloyl morpholine, N-(meta) acryloyl pyrrolidone, N-(meta) acryloyl caprolactam, acrylic acid (meta) poly (aminoethyl), etc. can use it typically.

[0018]As for the content of amino alkyl (meta) acrylate, 0.1 % of the weight - 30 % of the weight or less are preferred.

[0019]When it was less than 0.1 % of the weight and pastes up with glass, probably because a polar effect is spoiled, An adhesive property, an adhesive property if especially an adhesive property with glass becomes insufficient, and 30 % of the weight is exceeded, probably because softening temperature will become low, and handling nature (anti-blocking nature) get worse, and coloring (yellowing), weatherability, and a water resisting property fall further easily.

[0020]In addition, it is also possible to carry out copolymerization of the various monomers according to the performance demanded suitably. For example, if heat resistance is required, copolymerization of acrylic acid (meta), the hydroxyethyl (meta) acrylate, etc. will be carried out, It is also possible to add polyisocyanate, melamine, etc. independently and they to stiffen a cross linking agent, or to carry out copolymerization of ethyl acrylate, the butyl acrylate, etc., if plasticity is required.

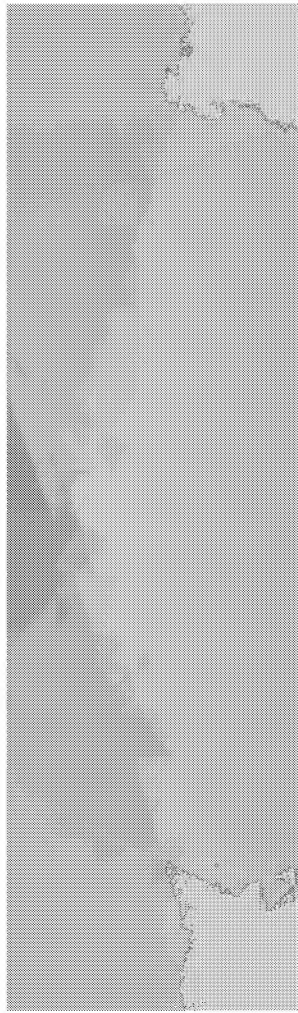
[0021]It is possible to add an antioxidant, paints, an ultraviolet ray absorbent, etc. in an adhesive film in the range which does not spoil an adhesive property and transparency.

[0022]Make it dissolve into an organic solvent and formation of an adhesive film applies above-mentioned adhesives to the surface of glass or a fluororesin sheet uniformly, The method of carrying out afterbaking, and making it dry and forming a tunic directly, the method of applying an adhesives solution uniformly on the substrate of detachability, making dry it, transferring by thermal melting arrival with a fluororesin sheet after that, and forming, etc. are possible.

[0023]When there is a possibility that a wrinkle may enter on the surface of a fluororesin sheet when forming an adhesive film in a fluororesin sheet, If there is also a method of making a detachability substrate exfoliate and the substrate of detachability is used in the case of formation of a fluororesin sheet after laminating the substrate of detachability at the back of a fluororesin sheet, giving the "waist" and forming an adhesive film, it can use as it is.

[0024]In forming an adhesive film on the surface of a fluororesin sheet, Since the adhesive property of a fluororesin sheet and an adhesive film is raised, the surface of a fluororesin sheet can also be beforehand etched or oxidized by methods, such as corona discharge treatment, plasma discharge processing, and sodium AMMONIUA processing.

[0025]In order to obtain the glass layered product of this invention, said adhesive film can be formed on the surface of glass, said adhesive film can be formed in the method of carrying out heat crimping to a fluororesin sheet, and making it weld, or the fluororesin sheet surface, and it can be based on the method of carrying out application-of-pressure sticking by pressure at glass,



and making this welding.

[0026] And the glass layered product obtained is that the layered product which was excellent in transparency and adhesive strength, and had high fire retardancy can also be manufactured.

[0027]

[Example] Hereafter, an example explains this invention still more concretely.

(Example 1) 40 % of the weight of vinylidene fluorides, 20 % of the weight of hexafluoropropylene, and the copolymerization fluoro-resin that consists of 40 % of the weight of tetrafluoroethylenes were extruded with the extrusion machine, and the 200-micron-thick fluororesin sheet was obtained.

[0028] And the acrylic ester copolymer which consists of N, 5 % of the weight of N dimethylamino ethyl acrylate, and 95 % of the weight of methyl methacrylate was dissolved in the organic solvent (toluene: MEK=2:1) as adhesives, and it applied by the coating machine on the fluororesin sheet. Subsequently, it heated for 30 seconds with a 100 °C heating furnace, the solvent was dried and removed, the 2-micron-thick adhesive film was formed in fluororesin sheet one side, and the sheet for glass lamination was obtained. Adhesive evaluation was performed with the following valuation method using this sheet. The result is shown in Table 1. (Valuation method)

The fluororesin sheet was piled up so that an adhesive film might turn to a glass surface, and it pasted together to soda glass with a production thickness of 3 mm (a size, 150 mm x 50 mm) of the evaluation (1) sample of adhesive strength by performing application-of-pressure heating for 5 minutes on condition of 140 °C and 2kg/cm<sup>2</sup> with the heat pressing machine.

(2) In [ put two notches into the surface of the fluororesin sheet which the normal-state strong degree stuck at intervals of 18 mm, and ] 23 °C in parallel with the direction of a notch the fluororesin sheet between the notch, It removed by speed 5 mm/min at the angle of 180 degrees, and adhesive strength at that time (gf/18mm) was made into normal-state intensity.

(3) After pasting together on condition of the voile intensity above, it soaked into 100 °C boiling water for 2 hours, and took out, and adhesive strength measured similarly was made into voile intensity. (Example 2) It evaluated like Example 1 except having used the acrylic ester copolymer which consists of 2 % of the weight of methacrylic acid poly (aminoethyl), 80 % of the weight of methyl methacrylate, and 18 % of the weight of butyl acrylate. A result is shown in Table 1.

(Comparative example 1) It evaluated like Example 1 except having used polymethylmethacrylate as adhesives. A result is shown in Table 1.

(Comparative example 2) It evaluated like Example 1 except having used the acrylic ester copolymer which consists adhesives of 3 % of the weight of acrylic acid, and 97 % of the weight of methylmetaacrylates. A result is shown in Table 1.

(Comparative example 3) As opposed to acrylic ester copolymer 100 weight section which consists of 1 % of the weight of methacrylic acid, 2 % of the weight of hydroxyethyl acrylate, 90 % of the weight of methylmetaacrylates, and 7 % of the weight of butyl acrylate as adhesives, It evaluated like Example 1 except having used the adhesives which blended hexamethylene diisocyanate 5 weight section. A result is shown in Table 1.

[0029]

[Table 1]

実施例、比較例	接着強度 (gf/18mm)		判定
	常 態	ボイル後	
実施例 1	1300	1200	○
実施例 2	1700	1100	○
比較例 1	340	20	×
比較例 2	410	0	×
比較例 3	600	10	×

[0030]

[Effect of the Invention] According to this invention, the fluororesin sheet the glass layered product which firm adhesive strength was obtained at, and was extremely excellent also in the fragment preventing scattering effect, and was excellent in fire prevention and flame-resistance, and for glass \*\* Li doubling can be provided.

[Translation done.]